Hydrated-Electron Relaxation Dynamics Studied with 5-fs Pulses

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10.30 QFG1

Hydrated-Electron Relaxation Dynamics Studied with 5-fs Pulses

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Excess electrons in condensed-phase media play a crucial role in the dynamics of important chemical processes. Among those are solution photochemistry, non-radiative electronic transitions, and charge transfer reactions. Hydrated electrons, i.e. electrons solvated in water, are of special interest. They can be viewed as an exceptional instrument for extracting information about the solvation process in water that plays an outstanding role in nature. Another motivation for a detailed study of the hydrated electron stems from the unique possibility to confront the predictions of mixed classical-quantum mechanical molecular dynamics simulations. This presents a direct way to verify the basic *a priori* assumptions that radically influence the outcome of computer modeling.

In this Contribution we present an experimental study of the energy relaxation of the photo-excited hydrated electron. The results of frequency-resolved pump-probe with 5-fs pulses provide sufficient evidence in support of an extremely fast initial energy relaxation. Our data show that this process is controlled by librations of the surrounding water molecules and has a decay time of ~50 fs. We further demonstrate that the subsequent cooling of the hot-ground state proceeds on a ps time scale and exhibits no isotope effect.

The overview of the fit results of the experimental transient spectra is shown in Fig.1. The contribution of the stimulated emission becomes insignificant after first 100 fs due to depletion of the excited state (open circles). The frequency of the excited-ground state crossing point is ~9500 cm^{-1} which corresponds to ~2/3 of the initial excitation frequency. Therefore, a large amount of energy deposited on the hydrated electron is rapidly absorbed by the water molecules with the characteristic transfer time of ~50 fs. In accordance with our previous findings [1,2], this decay time is dominated by the librations of water molecules as concluded from a substantial isotope effect.

The following relaxation occurs in the hot ground state with a characteristic time of 1 ps (Fig.1b). At this stage the water molecules surrounding the electron transfer the accumulated energy into a collective-type translational motion, most probably via the existing hydrogen-bond network. Finally, a nearly full equilibration of the hydrated electron is achieved by ~6 ps.

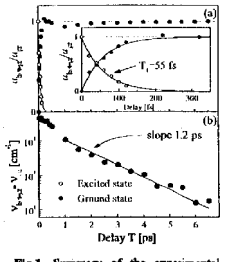

Fig.1. Summary of the experimental results: relative amplitudes of the excited (open circles) and hot ground (solid circles) states (a) and the spectral shift of the peak of the hot ground-state absorption with respect to the initial transition frequency (b). Solid curves in the inset show a mono-exponential decay and rise with a 55-fs time constant.

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10.45 QFG2

Decay Times of Surface Plasmon Excitation in Metal Nanoparticles Determined by Laser-induced Persistent Spectral Hole Burning

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Surface plasmon excitation in small metal particles has found great interest in the past, in particular since this collective oscillation of the conduction electrons can be stimulated with light and since its resonance frequency can be tuned over a wide spectral range by varying the size and shape of the clusters, by changing the dielectric surrounding and choosing different metals. Even though numerous investigations on SP's have been reported, no systematic investigation of the decay time T_2 and the decay mechanisms of SP excitation are available. Main reason is that nanoparticles usually have a broad size and shape distribution which introduces inhomogeneous line broadening and prevents the determination of T_2 by linear optical spectroscopy and time resolved experiments using femtosecond laser pulses [1,2].

Here, we describe a novel technique to determine the homogeneous linewidths of surface plasmon resonances of metal nanoparticles in the presence of inhomogeneous broadening and thus measure T_2. The method is based on spectral hole burning in the inhomogeneously broadenend absorption profiles of metal nanoparticles and has been applied to supported oblate Ag clusters with radii of 7.5 nm. From the experimental results and a theoretical model of hole burning the linewidth of 260 meV corresponding to a decay time of 4.8 fs was extracted. This value is *shorter* than expected for damping by bulk electron scattering. We conlcude that additional damping mechanisms, in particular surface scattering, come into play if the electrons are confined in particles with sizes below 10 nm. Furthermore, an influence of the shape of the clusters on the decay time was observed.

The technique presented here holds great promise for investigating SP's as a function of particle radius, an essential step towards a detailed understanding of the importance of different decay mechanisms. This is also essential to optimize the local field enhancement at the particle surface in a systematic way by generation of aggregates with optimum axial ratio and by precise control of the chemical surrounding including choice of the substrate material.

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